Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis[2-(4-bromobenzyl)isoquinolinium] bis(1,2-dicyanoethene-1,2-dithiolato-κ^2S,S')nickel(II)

Ai-Qun Zhou,[a] Jia-Rong Zhou[b] and Chun-Lin Ni[b]*

[a]Hunan College of Information, Hunan, Changsha 410200, People's Republic of China, and [b]Department of Applied Chemistry, College of Science, South China Agricultural University, Guangzhou 510642, People's Republic of China
Correspondence e-mail: ctgunicl@163.com

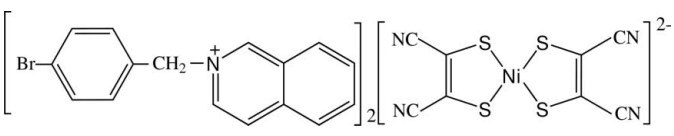
Received 31 October 2007; accepted 5 November 2007

Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.011 Å; R factor = 0.065; wR factor = 0.147; data-to-parameter ratio = 14.7.

The new title nickel(II) complex, $(C_{16}H_{13}BrN)_2[Ni(C_4N_2S_2)_2]$, is a salt obtained by the direct reaction of $NiCl_2$, disodium maleonitriledithiolate (Na_2mnt) and 1-(4-bromobenzyl)-isoquinolinium bromide, $(BrBzIQl)^+Br^-$, in methanol. The structure contains two $(BrBzIQl)^+$ cations and an $Ni(mnt)_2^{2-}$ anion in the asymmetric unit. In the two $(BrBzIQl)^+$ cations, the dihedral angles between the benzene ring and the isoquinoline plane are 71.0 (4) and 82.1 (4)°. The $[Ni(mnt)_2]^{2-}$ anion exhibits a slightly distorted square-planar coordination geometry. The crystal structure is stabilized by three weak C—H···N hydrogen bonds and a π–π stacking interaction involving the benzene ring and isoquinoline plane [centroid–centroid separation 3.774 (2) Å]

Related literature

For details of other square-planar 1,2-dithiolene metal complexes, see: Robertson & Cronin (2002); Ni *et al.* (2005); Xie *et al.* (2002); Ren *et al.* (2002); Nishijo *et al.* (2003); Canadell (1999). For the structures of related $Ni(mnt)_2^-$ complexes with square-planar geometry and a substituted isoquinolinium counter-ion, see: Ni, Dang *et al.* (2005) Ni, Yang & Meng (2005), Ni *et al.* 2006, 2007).



Experimental

Crystal data

$(C_{16}H_{13}BrN)_2[Ni(C_4N_2S_2)_2]$
M_r = 937.44
Triclinic, $P\overline{1}$
a = 11.320 (4) Å
b = 13.354 (5) Å
c = 14.754 (5) Å
α = 110.776 (7)°
β = 101.261 (6)°
γ = 97.880 (7)°
V = 1992.8 (12) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.74 mm^{-1}
T = 291 (2) K
0.30 × 0.30 × 0.10 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.461, T_{max} = 0.762
9888 measured reflections
6871 independent reflections
3408 reflections with $I > 2\sigma(I)$
R_{int} = 0.085

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.147
S = 1.04
6871 reflections
466 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.96 e Å^{-3}
$\Delta\rho_{min}$ = −0.68 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C17—H17···N1^{i}	0.93	2.40	3.226 (10)	148
C31—H31A···N2^{ii}	0.97	2.48	3.359 (10)	151
C36—H36···N2^{iii}	0.93	2.59	3.288 (9)	132

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y, -z+1$; (iii) $x-1, y, z+1$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors thank the Science and Technology Project (No. 2007B011000008) of Guangdong Science and Technology Department and the President's Science Foundation of South China Agricultural University (No. 2005 K092) for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2407).

References

Bruker (2000). *SHELXTL*. Version 5.0. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2001). *SMART* (Version 5.62) and *SAINT* (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.
Canadell, E. (1999). *Coord. Chem. Rev.* **185–186**, 629–651.
Ni, C. L., Dang, D. B., Li, Y. Z., Gao, S., Ni, Z. P., Tian, Z. F. & Meng, Q. J. (2005). *J. Solid State Chem.* **178**, 100-105.
Ni, C. L., Tian, Z. F., Ni, Z. P., Dang, D. B., Li, Y. Z., Song, Y. & Meng, Q. J. (2006). *Inog. Chim. Acta*, **359**, 3927–3933.
Ni, C. L., Yang, L. M. & Meng, Q. J. (2005). *Inorg. Chem. Commun.* **8**, 1105–1108.
Ni, C. L., Zhou, J. R., Tian, Z. F., Ni, Z. P., Li, Y. Z. & Meng, Q. J. (2007). *Inorg. Chem. Commun.* **10**, 880–883.
Nishijo, J., Ogura, E., Yamaura, J., Miyazaki, A., Enoki, T., Takano, T., Kuwatani, Y. & Iyoda, M. (2003). *Synth. Met.* **133–134**, 539–542.
Ren, X. M., Meng, Q. J., Song, Y., Lu, C. S. & Hu, C. J. (2002). *Inorg. Chem.* **41**, 5686–5692.
Robertson, N. & Cronin, L. (2002). *Coord. Chem. Rev.* **227**, 93–127.
Sheldrick, G. M. (2004). *SADABS*. University of Göttingen, Germany.
Xie, J. L., Ren, X. M., Song, Y., Zhang, W. W., Liu, W. L., He, C. & Meng, Q. J. (2002). *Chem. Commun.* pp. 2346–2347.

  doi:10.1107/S1600536807055821

supplementary materials

Acta Cryst. (2007). E**63**, m2980 [**doi:10.1107/S1600536807055821**]

Bis[2-(4-bromobenzyl)isoquinolinium] bis(1,2-dicyanoethene-1,2-dithiolato-κ^2S,S')nickel(II)

A.-Q. Zhou, J.-R. Zhou and C.-L. Ni

Comment

1,2-Dithiolene metal complexes are important molecular materials with interesting physical properties such as electical conductivity, superconductivity, photoelectric and magnetic properties (Robertson & Cronin, 2002; Ni *et al.*, 2004; Xie *et al.*, 2002; Ren *et al.*, 2002; Nishijo *et al.*, 2003; Canadell, 1999). Recently, some substituted isoquinolinium cations have been introduced into the $Ni(mnt)_2$ system to obtain $Ni(mnt)_2^{2-}$-based molecular solids showing unusual magnetic properties (Ni *et al.*, 2005; Ni *et al.*, 2006; Ni *et al.*, 2007). To gain more insight into how the substituted groups affects the stacking mode of $Ni(mnt)_2^{2-}$ anion, we herein present a new $Ni(mnt)_2^{2-}$ salt containing the 1-(4-bromobenzyl)isoquinolinium cation as shown in Fig.1. The salt consists of two $(BrBzIQl)^+$ cations and a $Ni(mnt)_2^{2-}$ anion in the asymmetric unit. In the cations, the dihedral angles between the benzene rings and the isoquinoline groups are 71.0 (4) ° for the cation containing N5, and 82.1 (4) ° for the cation containing N6. The Ni(II) ion of the $[Ni(mnt)_2]^{(2-)}$ anion and exhibits a slightly distorted square-planar coordination geometry. The four CN groups of $[Ni(mnt)_2]^{2-}$ are slightly tipped out of the S1/S2/Ni1/S3/S4 plane and the deviations from the plane are −0.294 (3) Å for N1, −0.324 (3) Å for N2, −0.237 (3) Å for N3 and 0.195 (3)Å for N4, respectively.

The crystal structure is stabilized by C17—H17···N1, C31—H31A···N2 and C36—H36···N2 hydrogen bonds, Table 1, and a π···π stacking interaction between the N5/C16···C24 group and the $C25^{i}$···$C30^{i}$ ring [Symmetry Code:(i)1 − *x*,1 − *y*,1 − *z*] with a distance of 3.774 (2) Å between the centroids of the two systems, Fig 2.

Experimental

The title compound was prepared by the direct reaction of $NiCl_2{\cdot}6H_2O$, Na_2mnt and $(BrBzIQl)^+Br^-$ in in methanol. The brown block-like single crystals were obtained by slow evaporation of a mixed solution of CH_3CN and i-PrOH (1:1) at room temperature for about two weeks.

Refinement

All H-atoms were positioned geometrically and refined using a riding model with d(C—H) = 0.93 Å, U_{iso}=1.2U_{eq} (C) for aromatic and 0.97 Å, U_{iso} = 1.2U_{eq} (C) for CH_2 atoms.

Figures

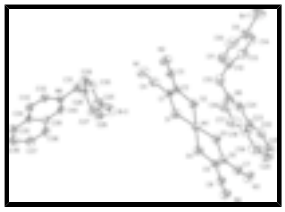


Fig. 1. The molecular structure of (I), with atom labels and 30% probability displacement ellipsoids for non-H atoms.

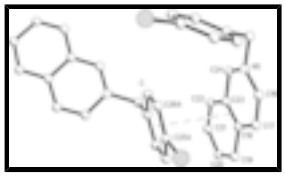


Fig. 2. The π···π interaction in the structure of (I) [Symmetry Code:(A)1 − *x*,1 − *y*,1 − *z*].

Bis[2-(4-bromobenzyl)isoquinolinium] bis(1,2-dicyanoethene-1,2-dithiolato-κ^2*S*,*S*')nickel(II)

Crystal data

$(C_{16}H_{13}BrN)_2[Ni(C_4N_2S_2)_2]$	$Z = 2$
$M_r = 937.44$	$F_{000} = 940$
Triclinic, $P\overline{1}$	$D_x = 1.562$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 11.320$ (4) Å	Cell parameters from 698 reflections
$b = 13.354$ (5) Å	$\theta = 2.8$–20.4º
$c = 14.754$ (5) Å	$\mu = 2.74$ mm^{-1}
$\alpha = 110.776$ (7)º	$T = 291$ (2) K
$\beta = 101.261$ (6)º	Block, brown
$\gamma = 97.880$ (7)º	0.30 × 0.30 × 0.10 mm
$V = 1992.8$ (12) Å^3	

Data collection

Bruker SMART APEX CCD diffractometer	6871 independent reflections
Radiation source: fine-focus sealed tube	3408 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.085$
$T = 291(2)$ K	$\theta_{max} = 25.0$º
φ and ω scans	$\theta_{min} = 1.9$º
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	$h = -13\rightarrow13$
$T_{min} = 0.461$, $T_{max} = 0.762$	$k = -15\rightarrow9$
9888 measured reflections	$l = -14\rightarrow17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.066$

$wR(F^2) = 0.147$

$S = 1.04$

6871 reflections

466 parameters

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.96$ e Å^{-3}

$\Delta\rho_{min} = -0.68$ e Å^{-3}

Extinction correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.32855 (7)	0.37256 (6)	0.16612 (5)	0.0583 (2)
Br1	1.19531 (9)	0.73115 (8)	0.60159 (10)	0.1871 (6)
Br2	0.17434 (9)	0.03355 (11)	0.37778 (7)	0.1603 (5)
C1	0.4413 (5)	0.2335 (4)	0.2708 (4)	0.0585 (16)
C2	0.4826 (5)	0.2076 (4)	0.1883 (4)	0.0562 (15)
C3	0.5536 (6)	0.1275 (5)	0.1648 (4)	0.0650 (17)
C4	0.4693 (6)	0.1786 (6)	0.3371 (5)	0.0705 (18)
C5	0.1738 (5)	0.5346 (5)	0.1360 (5)	0.0657 (17)
C6	0.2167 (5)	0.5077 (4)	0.0552 (5)	0.0617 (17)
C7	0.1943 (7)	0.5541 (5)	−0.0193 (5)	0.0727 (19)
C8	0.0952 (6)	0.6130 (5)	0.1550 (5)	0.0761 (19)
C9	1.0375 (8)	0.6558 (6)	0.5121 (8)	0.107
C10	0.9467 (8)	0.6324 (6)	0.5551 (5)	0.099 (3)
H10	0.9625	0.6513	0.6241	0.119*
C11	0.8294 (7)	0.5790 (6)	0.4910 (6)	0.096 (2)
H11	0.7654	0.5617	0.5177	0.115*
C12	0.8059 (7)	0.5513 (5)	0.3897 (6)	0.0724 (19)
C13	0.9011 (8)	0.5752 (6)	0.3523 (5)	0.089 (2)
H13	0.8880	0.5555	0.2834	0.106*
C14	1.0172 (7)	0.6285 (6)	0.4156 (7)	0.102 (2)
H14	1.0818	0.6451	0.3890	0.122*
C15	0.6783 (6)	0.4941 (5)	0.3214 (5)	0.097 (2)
H15A	0.6850	0.4467	0.2563	0.117*
H15B	0.6365	0.4483	0.3493	0.117*
C16	0.5567 (9)	0.6257 (8)	0.3865 (7)	0.119 (3)
H16	0.5716	0.6073	0.4422	0.143*
C17	0.4902 (8)	0.7017 (8)	0.3868 (6)	0.124 (3)
H17	0.4604	0.7362	0.4416	0.148*
C18	0.4681 (7)	0.7266 (6)	0.3041 (7)	0.092 (2)
C19	0.3982 (8)	0.8111 (7)	0.3006 (7)	0.118 (3)
H19	0.3682	0.8494	0.3540	0.141*
C20	0.3801 (8)	0.8300 (6)	0.2136 (8)	0.107 (3)
H20	0.3358	0.8820	0.2075	0.129*
C21	0.4259 (7)	0.7737 (7)	0.1355 (6)	0.094 (2)

H21	0.4125	0.7901	0.0787	0.113*
C22	0.4893 (6)	0.6959 (6)	0.1375 (6)	0.084 (2)
H22	0.5174	0.6578	0.0828	0.101*
C23	0.5108 (6)	0.6752 (5)	0.2229 (6)	0.0746 (19)
C24	0.5810 (6)	0.5931 (5)	0.2271 (6)	0.079 (2)
H24	0.6096	0.5548	0.1727	0.095*
C25	0.1943 (7)	0.0626 (7)	0.5152 (5)	0.095
C26	0.1321 (7)	0.1321 (6)	0.5688 (6)	0.100 (2)
H26	0.0813	0.1661	0.5376	0.120*
C27	0.1436 (6)	0.1519 (5)	0.6671 (6)	0.084 (2)
H27	0.0971	0.1961	0.7019	0.100*
C28	0.2237 (5)	0.1071 (4)	0.7157 (5)	0.0587 (15)
C29	0.2878 (6)	0.0399 (5)	0.6612 (5)	0.0728 (18)
H29	0.3408	0.0077	0.6926	0.087*
C30	0.2760 (6)	0.0186 (5)	0.5605 (5)	0.087 (2)
H30	0.3227	−0.0247	0.5250	0.104*
C31	0.2412 (6)	0.1313 (5)	0.8254 (4)	0.0690 (17)
H31A	0.3078	0.1000	0.8478	0.083*
H31B	0.2649	0.2103	0.8631	0.083*
C32	0.0844 (6)	−0.0256 (5)	0.8057 (4)	0.0639 (17)
H32	0.1244	−0.0715	0.7649	0.077*
C33	−0.0166 (6)	−0.0677 (5)	0.8254 (4)	0.0648 (17)
H33	−0.0463	−0.1435	0.7965	0.078*
C34	−0.0797 (5)	−0.0037 (5)	0.8871 (4)	0.0528 (15)
C35	−0.1846 (6)	−0.0443 (5)	0.9091 (4)	0.0673 (18)
H35	−0.2181	−0.1196	0.8817	0.081*
C36	−0.2396 (6)	0.0265 (6)	0.9718 (5)	0.0749 (19)
H36	−0.3104	−0.0011	0.9862	0.090*
C37	−0.1891 (6)	0.1402 (6)	1.0139 (5)	0.0757 (19)
H37	−0.2258	0.1873	1.0570	0.091*
C38	−0.0882 (6)	0.1812 (5)	0.9925 (4)	0.0687 (17)
H38	−0.0564	0.2568	1.0201	0.082*
C39	−0.0302 (6)	0.1117 (5)	0.9290 (4)	0.0549 (15)
C40	0.0727 (6)	0.1510 (5)	0.9056 (4)	0.0563 (15)
H40	0.1046	0.2265	0.9327	0.068*
N1	0.4949 (6)	0.1342 (5)	0.3877 (4)	0.095 (2)
N2	0.6105 (6)	0.0614 (5)	0.1465 (4)	0.097 (2)
N3	0.1829 (6)	0.5868 (5)	−0.0815 (5)	0.093 (2)
N4	0.0365 (6)	0.6768 (5)	0.1724 (5)	0.098 (2)
N5	0.6030 (5)	0.5746 (5)	0.3085 (6)	0.0826 (17)
N6	0.1288 (4)	0.0869 (4)	0.8465 (3)	0.0573 (12)
S1	0.35194 (16)	0.32994 (13)	0.29755 (11)	0.0708 (5)
S2	0.44630 (15)	0.26760 (12)	0.10251 (11)	0.0654 (5)
S3	0.31046 (15)	0.41468 (12)	0.03658 (11)	0.0676 (5)
S4	0.20597 (17)	0.47605 (14)	0.22340 (13)	0.0810 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0551 (5)	0.0450 (5)	0.0682 (5)	0.0130 (3)	0.0170 (4)	0.0135 (3)
Br1	0.1028 (7)	0.0784 (7)	0.2734 (14)	0.0060 (5)	−0.0676 (8)	0.0123 (7)
Br2	0.1135 (8)	0.2950 (15)	0.0978 (7)	0.0386 (9)	0.0250 (6)	0.1107 (8)
C1	0.052 (4)	0.055 (4)	0.059 (4)	0.012 (3)	0.010 (3)	0.014 (3)
C2	0.048 (4)	0.051 (4)	0.061 (4)	0.009 (3)	0.010 (3)	0.014 (3)
C3	0.066 (4)	0.078 (5)	0.066 (4)	0.031 (4)	0.029 (3)	0.034 (3)
C4	0.067 (5)	0.078 (5)	0.064 (5)	0.022 (4)	0.014 (4)	0.025 (4)
C5	0.055 (4)	0.055 (4)	0.082 (5)	0.015 (3)	0.016 (3)	0.021 (3)
C6	0.064 (4)	0.036 (3)	0.069 (4)	0.007 (3)	0.008 (3)	0.009 (3)
C7	0.087 (5)	0.049 (4)	0.072 (5)	0.020 (4)	0.013 (4)	0.014 (4)
C8	0.079 (5)	0.064 (5)	0.097 (5)	0.028 (4)	0.035 (4)	0.035 (4)
C9	0.076	0.085	0.121	0.014	−0.011	0.015
C10	0.111 (7)	0.079 (5)	0.078 (5)	0.035 (5)	0.001 (5)	0.004 (4)
C11	0.089 (6)	0.107 (6)	0.089 (6)	0.022 (5)	0.023 (5)	0.035 (5)
C12	0.074 (5)	0.046 (4)	0.083 (5)	0.009 (3)	0.009 (4)	0.016 (3)
C13	0.087 (6)	0.092 (6)	0.085 (5)	0.026 (5)	0.022 (5)	0.031 (4)
C14	0.074 (6)	0.093 (6)	0.143 (7)	0.019 (5)	0.031 (5)	0.051 (5)
C15	0.088 (5)	0.054 (4)	0.119 (6)	0.001 (4)	−0.005 (5)	0.020 (4)
C16	0.126 (8)	0.132 (8)	0.105 (7)	0.049 (7)	0.036 (6)	0.043 (6)
C17	0.126 (8)	0.160 (9)	0.080 (6)	0.068 (7)	0.032 (6)	0.027 (6)
C18	0.083 (5)	0.087 (6)	0.080 (6)	0.017 (4)	0.013 (5)	0.009 (5)
C19	0.119 (7)	0.105 (7)	0.099 (7)	0.045 (6)	0.019 (6)	0.003 (5)
C20	0.094 (6)	0.084 (6)	0.118 (7)	0.029 (5)	0.008 (6)	0.016 (6)
C21	0.079 (5)	0.081 (6)	0.110 (6)	0.010 (5)	0.014 (5)	0.032 (5)
C22	0.065 (5)	0.084 (6)	0.093 (6)	0.008 (4)	0.020 (4)	0.026 (4)
C23	0.064 (4)	0.054 (4)	0.079 (5)	−0.003 (4)	0.009 (4)	0.007 (4)
C24	0.062 (5)	0.056 (5)	0.092 (6)	−0.003 (4)	0.006 (4)	0.011 (4)
C25	0.088	0.118	0.087	0.022	0.019	0.054
C26	0.099 (6)	0.128 (7)	0.121 (7)	0.052 (5)	0.033 (5)	0.090 (6)
C27	0.082 (5)	0.082 (5)	0.106 (6)	0.041 (4)	0.028 (5)	0.051 (4)
C28	0.053 (4)	0.050 (4)	0.076 (4)	0.012 (3)	0.016 (3)	0.028 (3)
C29	0.079 (5)	0.070 (5)	0.072 (5)	0.033 (4)	0.017 (4)	0.026 (3)
C30	0.083 (5)	0.108 (6)	0.073 (5)	0.036 (4)	0.022 (4)	0.034 (4)
C31	0.061 (4)	0.062 (4)	0.075 (5)	0.008 (3)	0.017 (3)	0.019 (3)
C32	0.066 (4)	0.048 (4)	0.072 (4)	0.015 (3)	0.013 (3)	0.018 (3)
C33	0.073 (5)	0.044 (4)	0.063 (4)	0.001 (3)	0.005 (4)	0.015 (3)
C34	0.057 (4)	0.053 (4)	0.044 (3)	0.006 (3)	−0.003 (3)	0.024 (3)
C35	0.062 (4)	0.069 (5)	0.059 (4)	−0.005 (4)	−0.002 (3)	0.027 (3)
C36	0.068 (5)	0.094 (6)	0.065 (4)	0.006 (4)	0.013 (4)	0.040 (4)
C37	0.080 (5)	0.084 (6)	0.077 (5)	0.026 (4)	0.031 (4)	0.039 (4)
C38	0.082 (5)	0.059 (4)	0.080 (5)	0.025 (4)	0.032 (4)	0.035 (3)
C39	0.063 (4)	0.049 (4)	0.059 (4)	0.016 (3)	0.015 (3)	0.029 (3)
C40	0.063 (4)	0.045 (4)	0.062 (4)	0.014 (3)	0.013 (3)	0.024 (3)
N1	0.115 (5)	0.106 (5)	0.081 (4)	0.054 (4)	0.029 (4)	0.044 (4)

N2	0.113 (5)	0.116 (5)	0.099 (4)	0.073 (4)	0.051 (4)	0.054 (4)
N3	0.124 (5)	0.072 (4)	0.083 (5)	0.035 (4)	0.015 (4)	0.030 (3)
N4	0.099 (5)	0.084 (4)	0.136 (5)	0.050 (4)	0.049 (4)	0.052 (4)
N5	0.064 (4)	0.065 (4)	0.097 (5)	0.004 (3)	0.009 (4)	0.017 (4)
N6	0.057 (3)	0.048 (3)	0.065 (3)	0.012 (3)	0.011 (3)	0.022 (3)
S1	0.0789 (12)	0.0677 (11)	0.0693 (11)	0.0304 (9)	0.0312 (9)	0.0198 (8)
S2	0.0724 (11)	0.0620 (10)	0.0691 (10)	0.0270 (9)	0.0271 (9)	0.0255 (8)
S3	0.0786 (11)	0.0489 (10)	0.0704 (10)	0.0211 (8)	0.0216 (9)	0.0143 (8)
S4	0.0877 (13)	0.0815 (13)	0.0977 (13)	0.0462 (11)	0.0460 (11)	0.0414 (10)

Geometric parameters (Å, °)

Ni1—S3	2.1571 (19)	C19—H19	0.9300
Ni1—S2	2.1657 (17)	C20—C21	1.373 (10)
Ni1—S4	2.1691 (18)	C20—H20	0.9300
Ni1—S1	2.186 (2)	C21—C22	1.346 (9)
Br1—C9	1.895 (8)	C21—H21	0.9300
Br2—C25	1.884 (7)	C22—C23	1.367 (9)
C1—C2	1.338 (7)	C22—H22	0.9300
C1—C4	1.430 (9)	C23—C24	1.450 (9)
C1—S1	1.729 (6)	C24—N5	1.296 (8)
C2—C3	1.411 (8)	C24—H24	0.9300
C2—S2	1.737 (6)	C25—C30	1.355 (9)
C3—N2	1.149 (7)	C25—C26	1.363 (10)
C4—N1	1.127 (7)	C26—C27	1.354 (8)
C5—C6	1.325 (8)	C26—H26	0.9300
C5—C8	1.453 (9)	C27—C28	1.377 (8)
C5—S4	1.737 (7)	C27—H27	0.9300
C6—C7	1.440 (9)	C28—C29	1.368 (7)
C6—S3	1.726 (6)	C28—C31	1.500 (7)
C7—N3	1.142 (7)	C29—C30	1.385 (8)
C8—N4	1.140 (7)	C29—H29	0.9300
C9—C14	1.302 (10)	C30—H30	0.9300
C9—C10	1.366 (11)	C31—N6	1.465 (7)
C10—C11	1.393 (9)	C31—H31A	0.9700
C10—H10	0.9300	C31—H31B	0.9700
C11—C12	1.365 (9)	C32—C33	1.332 (8)
C11—H11	0.9300	C32—N6	1.380 (6)
C12—C13	1.354 (9)	C32—H32	0.9300
C12—C15	1.506 (9)	C33—C34	1.393 (8)
C13—C14	1.379 (9)	C33—H33	0.9300
C13—H13	0.9300	C34—C35	1.382 (8)
C14—H14	0.9300	C34—C39	1.422 (7)
C15—N5	1.500 (8)	C35—C36	1.380 (8)
C15—H15A	0.9700	C35—H35	0.9300
C15—H15B	0.9700	C36—C37	1.404 (8)
C16—C17	1.343 (11)	C36—H36	0.9300
C16—N5	1.357 (9)	C37—C38	1.340 (8)
C16—H16	0.9300	C37—H37	0.9300

C17—C18	1.362 (10)	C38—C39	1.401 (8)
C17—H17	0.9300	C38—H38	0.9300
C18—C23	1.369 (9)	C39—C40	1.368 (7)
C18—C19	1.474 (10)	C40—N6	1.315 (6)
C19—C20	1.377 (10)	C40—H40	0.9300
S3—Ni1—S2	86.47 (7)	C22—C23—C18	123.5 (8)
S3—Ni1—S4	91.51 (7)	C22—C23—C24	118.3 (8)
S2—Ni1—S4	177.56 (8)	C18—C23—C24	118.2 (8)
S3—Ni1—S1	178.51 (7)	N5—C24—C23	118.3 (7)
S2—Ni1—S1	92.37 (7)	N5—C24—H24	120.8
S4—Ni1—S1	89.67 (7)	C23—C24—H24	120.8
C2—C1—C4	119.3 (6)	C30—C25—C26	120.9 (7)
C2—C1—S1	121.3 (5)	C30—C25—Br2	119.1 (6)
C4—C1—S1	119.4 (5)	C26—C25—Br2	119.9 (6)
C1—C2—C3	121.7 (5)	C27—C26—C25	120.6 (7)
C1—C2—S2	121.4 (5)	C27—C26—H26	119.7
C3—C2—S2	116.9 (4)	C25—C26—H26	119.7
N2—C3—C2	178.9 (7)	C26—C27—C28	120.4 (6)
N1—C4—C1	177.4 (8)	C26—C27—H27	119.8
C6—C5—C8	121.7 (6)	C28—C27—H27	119.8
C6—C5—S4	121.8 (5)	C29—C28—C27	118.1 (6)
C8—C5—S4	116.5 (5)	C29—C28—C31	120.7 (6)
C5—C6—C7	124.4 (6)	C27—C28—C31	121.2 (6)
C5—C6—S3	119.8 (5)	C28—C29—C30	121.9 (6)
C7—C6—S3	115.7 (5)	C28—C29—H29	119.0
N3—C7—C6	174.8 (8)	C30—C29—H29	119.0
N4—C8—C5	177.9 (8)	C25—C30—C29	117.9 (6)
C14—C9—C10	122.2 (7)	C25—C30—H30	121.0
C14—C9—Br1	121.9 (8)	C29—C30—H30	121.0
C10—C9—Br1	115.9 (8)	N6—C31—C28	112.1 (5)
C9—C10—C11	116.9 (7)	N6—C31—H31A	109.2
C9—C10—H10	121.6	C28—C31—H31A	109.2
C11—C10—H10	121.6	N6—C31—H31B	109.2
C12—C11—C10	121.7 (7)	C28—C31—H31B	109.2
C12—C11—H11	119.1	H31A—C31—H31B	107.9
C10—C11—H11	119.1	C33—C32—N6	119.3 (6)
C13—C12—C11	118.0 (7)	C33—C32—H32	120.4
C13—C12—C15	120.9 (7)	N6—C32—H32	120.4
C11—C12—C15	121.1 (8)	C32—C33—C34	123.2 (6)
C12—C13—C14	120.4 (7)	C32—C33—H33	118.4
C12—C13—H13	119.8	C34—C33—H33	118.4
C14—C13—H13	119.8	C35—C34—C33	124.9 (6)
C9—C14—C13	120.7 (8)	C35—C34—C39	119.2 (6)
C9—C14—H14	119.7	C33—C34—C39	116.0 (6)
C13—C14—H14	119.7	C36—C35—C34	120.1 (6)
N5—C15—C12	111.7 (5)	C36—C35—H35	119.9
N5—C15—H15A	109.3	C34—C35—H35	119.9
C12—C15—H15A	109.3	C35—C36—C37	120.2 (6)
N5—C15—H15B	109.3	C35—C36—H36	119.9

C12—C15—H15B	109.3	C37—C36—H36	119.9
H15A—C15—H15B	107.9	C38—C37—C36	120.5 (6)
C17—C16—N5	122.9 (9)	C38—C37—H37	119.8
C17—C16—H16	118.5	C36—C37—H37	119.8
N5—C16—H16	118.5	C37—C38—C39	120.8 (6)
C16—C17—C18	117.6 (8)	C37—C38—H38	119.6
C16—C17—H17	121.2	C39—C38—H38	119.6
C18—C17—H17	121.2	C40—C39—C38	122.2 (6)
C17—C18—C23	121.3 (8)	C40—C39—C34	118.6 (5)
C17—C18—C19	120.4 (9)	C38—C39—C34	119.2 (6)
C23—C18—C19	118.3 (8)	N6—C40—C39	123.0 (6)
C20—C19—C18	116.0 (8)	N6—C40—H40	118.5
C20—C19—H19	122.0	C39—C40—H40	118.5
C18—C19—H19	122.0	C24—N5—C16	121.5 (7)
C21—C20—C19	121.5 (9)	C24—N5—C15	122.3 (7)
C21—C20—H20	119.2	C16—N5—C15	116.2 (8)
C19—C20—H20	119.2	C40—N6—C32	119.9 (5)
C22—C21—C20	123.1 (8)	C40—N6—C31	121.7 (5)
C22—C21—H21	118.5	C32—N6—C31	118.4 (5)
C20—C21—H21	118.5	C1—S1—Ni1	102.3 (2)
C21—C22—C23	117.5 (7)	C2—S2—Ni1	102.5 (2)
C21—C22—H22	121.2	C6—S3—Ni1	104.1 (2)
C23—C22—H22	121.2	C5—S4—Ni1	102.6 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C17—H17···N1^{i}	0.93	2.40	3.226 (10)	148
C31—H31A···N2^{ii}	0.97	2.48	3.359 (10)	151
C36—H36···N2^{iii}	0.93	2.59	3.288 (9)	132

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+1, −*y*, −*z*+1; (iii) *x*−1, *y*, *z*+1.

Fig. 1

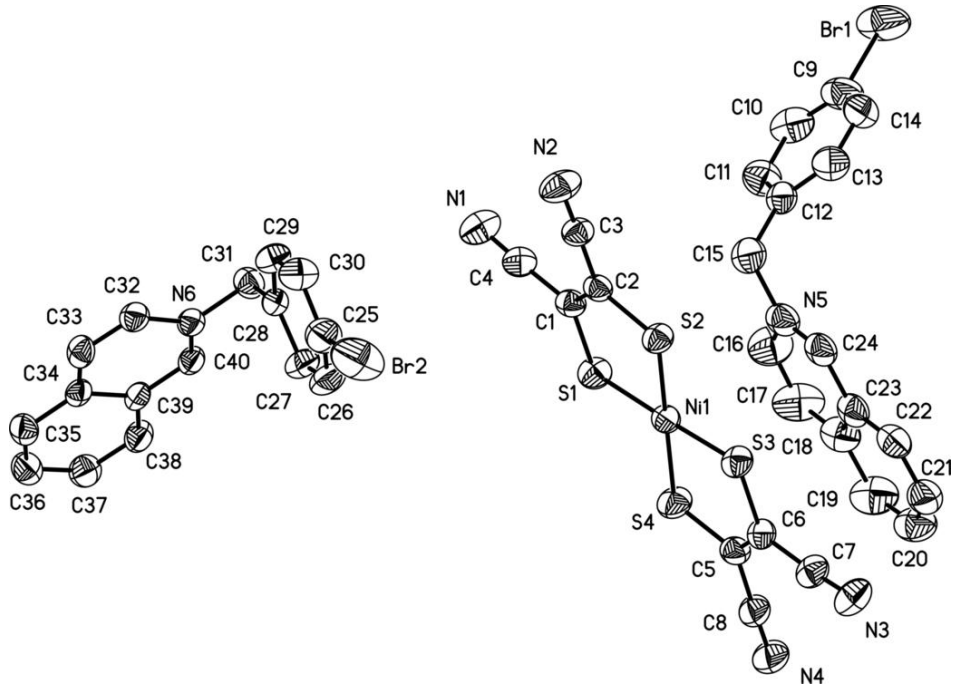

Br1
C9
C10
C14
N2
C11
C13
N1
C12
C3
C15
C4
C2
N5
C1
S2
C16
C24
C29
C31
C30
C32
N6
C25
C33
C28
Br2
C40
C34
C27
C26
C39
S1
Ni1
C17
C23
C22
C35
C38
S3
C18
C21
C36
C37
C19
S4
C6
C7
C20
C5
C8
N3
N4

Fig. 2